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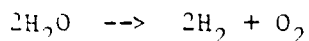
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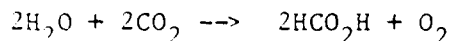
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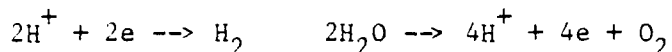
Many small molecule reactions that are candidates for light to chemical energy conversion such as water splitting,



or reactions involving carbon dioxide,



are redox reactions. As such they can be broken up into their component half reactions,



which immediately suggests the possibility of using excited state electron transfer chemistry to drive them.

The processes of importance in excited state electron transfer schemes depend upon the fundamental principles of chemistry and physics. From those principles, equations can be derived, which give quantitative or semiquantitative insight into quantum yields and rates. In turn, those equations are couched in terms of the molecular properties of the system. Between the underlying principles and an appropriate manipulation of properties, it does appear that it should be possible to dictate the rates and quantum yields of charge separation in molecular systems in a systematic way.

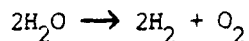
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ENERGY CONVERSION AT THE MOLECULAR LEVEL

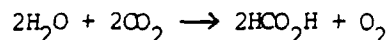
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INTRODUCTION

Many small molecule reactions that are candidates for light to chemical energy conversion such as water splitting,



or reactions involving carbon dioxide,

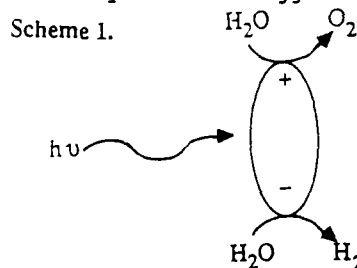


are oxidation-reduction reactions. As such, they can be broken up into their component half reactions,



which immediately suggests the possibility of using excited state electron transfer chemistry to drive them.¹⁻⁵

An approach based on molecular systems is suggested by Scheme 1.



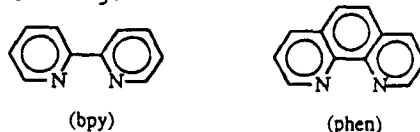
In Scheme 1 light absorption is followed by a series of electron transfer events which lead to spatially separated oxidative and reductive equivalents. Those equivalents, in turn, are utilized to drive separate catalysts for the oxidation or reduction of water.

The optical excitation-charge splitting sequence suggested in Scheme 1 is, of course, analogous to what happens at the reaction center in photosynthesis.⁶⁻⁸ The principles are available and processes are known at the molecular level which are required to build artificial systems which accomplish the same end. In a sequential order the processes that must occur are molecular light absorption, excited state electron transfer, electron transfer over

long distances, and electron transfer induced activation of molecular catalysts. The catalysts must have the ability to carry out complex multiple electron transfer reactions.

The theme here is to point to the fundamental principles that play an important role in the design of devices for optical excitation-charge splitting at the molecular level. The specific cases chosen as illustrations will come largely from our own work and the work of others based on metal to ligand charge transfer (MLCT) excited states. It is possible to find in these systems examples that nicely illustrate the interplay between fundamental principles and the design of molecular systems.

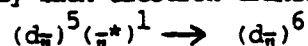
Excited State Decay. For the metal to ligand charge transfer (MLCT) excited states of complexes like $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy is 2,2'-bipyridine) $[(\text{bpy})\text{Re}(\text{CO})_3\text{Cl}]$, or $[\text{Os}(\text{phen})_3]^{2+}$ (phen is 1,10-phenanthroline) the change in



electronic configuration between the ground and excited states is,

$$(d_{\pi})^6 \xrightarrow{h\nu} (d_{\pi})^5(\pi^*)^1$$

The acceptor orbital is a vacant π^* orbital on the polypyridyl ligand. Temperature dependent lifetime and emission spectra measurements have revealed much about the properties of these excited states.^{9,10} They are typically weak emitters in fluid solution at room temperature, their lifetimes are dominated by nonradiative decay processes. In nonradiative decay the energy that is released by back electron transfer,



appears largely (> 90%) in polypyridyl based ring stretching modes and, to a lesser extent, in low frequency modes, including metal ligand stretching vibrations, and in the solvent.^{9,11,12}

From time dependent perturbation theory, the nonradiative decay rate constant, k_{nr} , is predicted to be proportional to the product of a vibrationally induced electronic coupling term and a "Franck-Condon" factor.^{12,13} To zero order the excited and ground state wave functions are orthogonal and can not mix. Vibrations of the

appropriate symmetry, the promoting modes, can increase orbital overlap which causes the states to mix.

The Franck-Condon factor is a mathematical function which describes how the energy released when electron transfer occurs is distributed amongst the various vibrational modes of the system.

An important development has been the utilization of the results of resonance Raman and emission spectral fitting to acquire the parameters required for the calculation of the Franck-Condon factors for the decay of MLCT excited states.^{11d,12,13g} The agreement between experiment and theory in this area shows that it is possible to learn how to control excited state properties systematically by taking advantage of physical insight. For example, theory predicts that k_{nr} should vary as the energy gap, E , as in eq. 1.¹²

$$k_{nr} \propto \exp(-\gamma E/\hbar\omega) \quad (1)$$

In eq. 1 $\hbar\omega$ is an averaged vibrational quantum spacing for the series of polypyridyl ring stretching modes which act as energy acceptors. γ is defined as,

$$\gamma = (\ln \frac{E}{S\hbar\omega}) - 1$$

S is the electron-vibrational coupling constant (Huang-Rhys factor).

It is related to the difference in equilibrium displacement in the averaged ν (bpy) mode between the ground and excited states.

Experimentally, it is possible to vary k_{nr} systematically by using changes in the ligands in complexes such as $[(bpy)Os(L)_4]^{2+}$ ($L = py, PR_3, CH_3CN, \dots$) to vary the energy gap.^{12,14}

The photochemistry of MLCT excited states is complicated by the appearance of other states such as dd states and higher lying MLCT states.^{14,15} However, the decay properties of the lowest MLCT states are very much in line with predictions based on fundamental physical principles: 1) The extent of the structural changes at the polypyridyl ligands in the excited states increases as the energy gap between states is increased. This is understandable since as the energy gap increases, mixing between the ground and excited states decreases. As the extent of mixing decreases the extent of charge transfer increases which causes the greater distortion in the excited state. 2) The same pattern of polypyridyl acceptor vibrations appears to dominate excited state

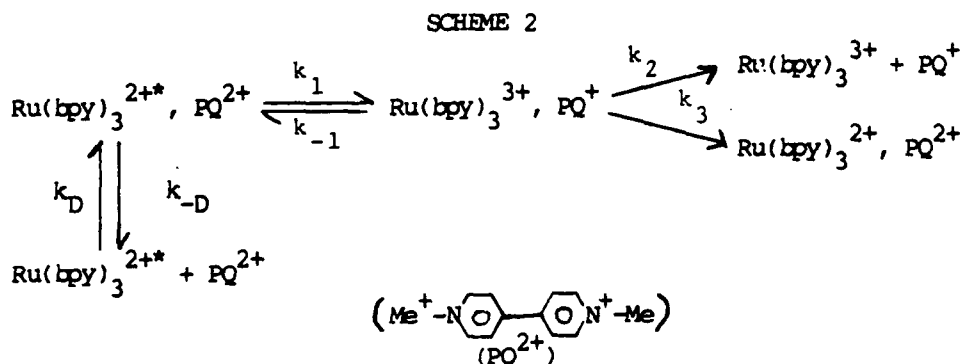
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decay where the acceptor ligand is of the type 4,4'-(X)₂-2,2'-bipyridine (X = NH₂, CH₃, H, C(O)OEt, ...).¹⁶ However, each ligand has its own individual nuances with S varying differently with the energy gap. 3) For complexes of Ru and Os where there are equivalent Franck-Condon factors, non-radiative decay is faster for Os by a factor of ~3 because greater spin-orbit coupling at Os ($\lambda_{Os} \sim 3000 \text{ cm}^{-1}$ vs. $\lambda_{Ru} \sim 1100 \text{ cm}^{-1}$) increases the magnitude of the vibrationally induced electronic coupling between states.

Spin effects play a role in both radiative and nonradiative decay. The lowest lying MLCT excited states are largely triplet $^3[(d_{\pi})^5(\pi^*)^1]$ in character and the ground state is a $(d_{\pi})^6$ singlet. The operators that mix them, the electric dipole moment operator for radiative decay $(\langle \psi_e | e\vec{r} | \psi_g \rangle)$ and the promoting mode $(\langle \psi_e | \partial/\partial q | \psi_g \rangle)$ for nonradiative decay, do not include spin. When spin-orbit coupling is included in the analysis, the "triplet" excited states mix with low lying singlet excited states. The matrix elements then become non-zero and provide the dynamic basis for excited state decay.

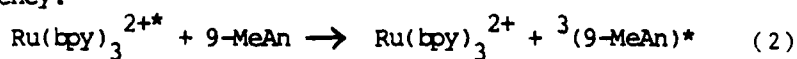
Excited State Electron Transfer. In an outer sphere excited state quenching scheme, there are a series of microscopic steps that occur before the redox products appear in solution. They are preassociation of the reactants, electron transfer quenching, and separation of the redox products. Separation is in competition with back electron transfer, Scheme 2.



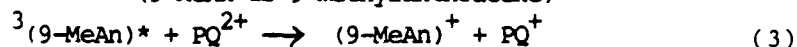
The role of free energy change (ΔG) in the electron transfer quenching step (k_1) has been well established and is in agreement

with the theoretical predictions of Hush and Marcus.¹⁷ In the classical limit, the maximum electron transfer rate is predicted to occur when $-\Delta G = \lambda$. λ is the sum of the intramolecular (λ_i) and solvent dipole orientational (λ_o) barriers to electron transfer. The yields of separated redox products depend upon the relative magnitudes of k_2 and k_3 in Scheme 2. k_2 is strongly influenced by electrostatic effects with the repulsion between like charged ions greatly favoring separation. The energy released in the back electron transfer step in Scheme 2 is considerable (~ 1.7 eV). In fact, the back electron transfer reaction is in the "inverted region" where $-\Delta G > \lambda$.¹⁸ In this region it is predicted theoretically that k_2 should decrease as the free energy stored in the quenching step is increased. In the limit that the energy released is much larger than λ , the electron transfer rate constant is predicted to have the same dependence on the energy gap as for nonradiative decay in eq. 1. Such effects play an important role in these systems where quantum efficiencies for the separation of redox products as high as unity have been achieved.¹⁹

Spin effects can also influence the magnitudes of separation efficiencies. An apparent example of this occurs in the excited state quenching of $[\text{Ru}(\text{bpy})_3]^{2+*}$ by PQ^{2+} . Under conditions of complete quenching, less than 20% of the excitation events lead to separated redox products.²⁰ By contrast, an indirect mechanism in which $[\text{Ru}(\text{bpy})_3]^{2+*}$ is initially quenched by energy transfer to an anthracene derivative, reaction 2, followed by electron transfer quenching of the anthracene, reaction 3, occurs with nearly unit efficiency.^{19b}



(9-MeAn is 9-methylantracene)



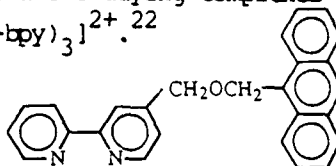
For the organic example in reaction 2 there is a spin prohibition to back electron transfer. The spin prohibition arises because of the differences in spin character between the triplet excited state and the singlet products,



The sequence k_1 followed by k_3 in Scheme 2 is closely related.

However, spin-orbit coupling at Ru is significant. The low lying "triplet" MLCT excited state has sufficient singlet character to break down the spin prohibition to electron transfer.²¹

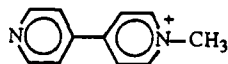
In an attempt to combine the virtues of the Ru-bpy visible light absorber and the spin advantage of electron transfer based on triplet anthracene, we are studying complexes of the type $[\text{Ru}(4\text{-Me-4'-(9-CH}_2\text{OCH}_2\text{An)-2,2'-bpy})_3]^{2+}$.²²



[4-Me-4'-(9-CH₂OCH₂An)-2,2'-bpy]

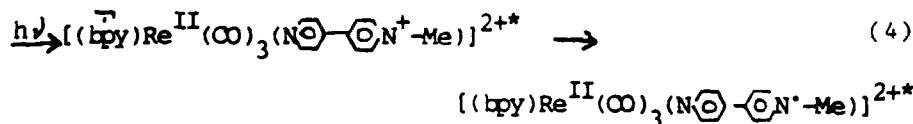
In this complex MLCT emission is essentially completely quenched. Triplet anthracene appears following MLCT excitation as shown by transient laser experiments.

Intramolecular analogs of the pyridinium quenching in Scheme 2 have also been prepared. In these complexes the effect of intramolecular structural changes can play a major role in rates of intramolecular electron transfer and can even dictate whether or not intramolecular electron transfer occurs. An example is the chromophore-quencher complex $[(\text{bpy})\text{Re}(\text{CO})_3(\text{MQ}^+)]^{2+}$.^{23,24}



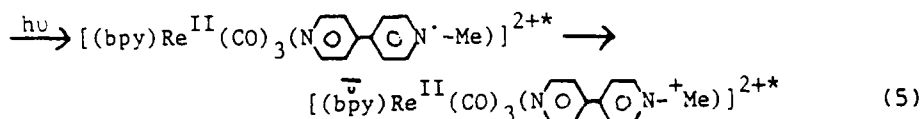
(MQ⁺)

An x-ray structural study of the PF_6^- salt of this complex has shown that the angle between the pyridyl rings of the pyridinium ligand is approximately 45° .²⁵ Spectroscopic studies suggest that an angle close to that is maintained in solution as well. The results of transient absorbance experiments show that following $\text{Re} \rightarrow \text{bpy}$ excitation of the complex, intramolecular electron transfer occurs to the pyridinium ligand, reaction 4



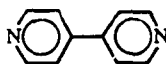
In the quenched product there is a flattening of the angle between the rings as shown by the appearance of typical reduced viologen

absorption bands in the transient absorbance experiments.^{23b} The driving force for flattening is the delocalization of the added electron over both rings. Spectroscopic studies show that the Re-bpy and Re-MQ⁺ based MLCT excited states lie close in energy. Upon vertical excitation the bpy-based state lies lowest. When the rings flatten, the MQ⁺-based state is stabilized by ~ 300 mV and it becomes the lowest excited state in fluid solution.²⁵ In a frozen 4:1 ethanol-methanol (V:V) glass at 77 K the vertical ordering of the states is maintained because of the inhibition to ring rotation in the glass. Emission is observed from the Re → bpy MLCT state even following Re → MQ⁺ excitation because the inversion in state ordering leads to reverse electron transfer,

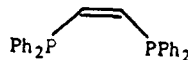


Whether or not intramolecular quenching occurs in these complexes can be manipulated by substituent effects.²⁶ In the sequence [(4,4'-(X)₂-bpy)Re(CO)₃(MQ⁺)]²⁺ (X = C(O)OEt, H, NH₂), the ester substituents lower the π*-bpy acceptor level and the state ordering is MLCT(Re-bpy) < MLCT(Re-MQ⁺). Intramolecular quenching does not occur even in fluid solution. For X = H the levels are closely matched. For X = NH₂ the energy of the π*(bpy) acceptor level is increased and intramolecular quenching occurs even in an EtOH-MeOH glass at 77K.

A closely related effect has been observed in the 4,4'-bipyridine (4,4'-bpy) bridged complex [(bpy)₂(CO)Os(4,4'-bpy)OsCl(phen)(cis-dppene)]³⁺ (phen is 1,10-phenanthroline).²⁷



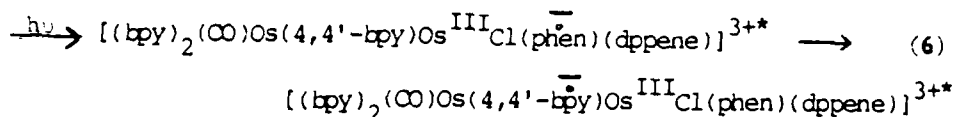
(4,4'-bpy)



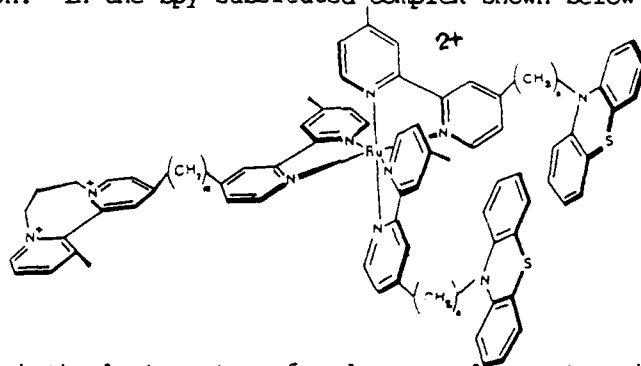
(cis-dppene)

For this complex Os → phen MLCT excitation in the glass at 77 K leads to emission only from the corresponding Os-phen MLCT excited states. However, transient absorbance experiments show that in fluid solution at room temperature initial MLCT excitation is

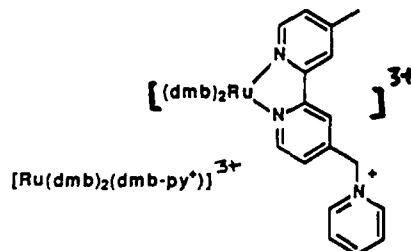
followed by intramolecular electron transfer to the 4,4'-bpy bridge. This was shown by the appearance of a reduced viologen like spectrum.



By adjusting the redox levels of appropriate donors and acceptors ΔG effects can be used to dictate the sequence of steps that occur in multiple electron transfer processes induced by optical excitation. In the bpy substituted complex shown below



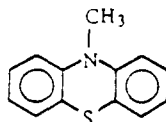
there are both electron transfer donors and acceptors bound to the MLCT chromophore.²⁸ The series of electron transfer events that lead to the charge separated state with reductive and oxidative equivalents stored on separate bpy ligands could be initiated by either initial reductive or oxidative electron transfer. Kinetic studies on model systems containing only the electron transfer donor or the electron transfer acceptor show that at room temperature both processes are very rapid. However, by adjusting the relative redox levels of donors and acceptors it is possible to utilize only one of the two processes to trigger the net electron transfer sequence. For example, in the complex,



(dmb is 4,4'-(CH₂)₂-2,2'-bipyridine)

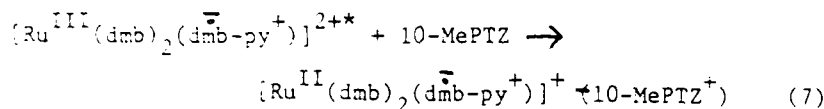
the chemically attached pyridinium ligand has a relatively low

potential as an electron acceptor, $E_{p,c}(\text{Mepy}^{+/0}) = -1.1 \text{ V}$ in 0.1 M $[\text{N}(\text{n-Bu})_4][\text{PF}_6]-\text{CH}_3\text{CN}$ vs. SSCE.²⁹ Optical excitation of the MLCT chromophore leads to negligible quenching. However, with added 10-methylphenothiazine,

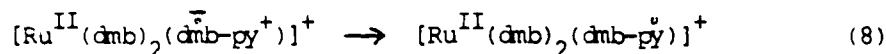


(10-MePTZ)

reductive electron transfer quenching occurs,



to give the bpy-localized reduction product. The bpy reduced product is enhanced as a reductant, -1.3 V compared to -0.8 V for the excited state. The enhanced reducing power triggers a now spontaneous intramolecular electron transfer to the pyridinium group, reaction 8.



Medium Effects. In normal electron transfer reactions, $-\Delta G < \lambda$. In this domain in the classical limit, the rate constant for intramolecular electron transfer varies with ΔG and λ as shown in eq. 9.

$$k = \nu_{\text{et}} \exp[-(\lambda + \Delta G)^2 / 4\lambda RT] \quad (9)$$

In eq. 9 the solvent plays a double role. It contributes to ΔG and to λ via the outer-sphere reorganization energy, λ_o . It can also help to dictate the pre-exponential term, ν_{et} , by solvent dynamics.³⁰

The effects on λ_o and ΔG lie in the change in electronic distribution between the initial and final states. In solution the surrounding solvent dipoles adopt the average equilibrium orientations appropriate to the electronic distributions of the two states. Differing degrees of interaction lead to the solvent

dependence of ΔG . For the transition between states to occur there is a requirement that solvent dipoles reorient. The reorientation is the origin of λ_0 . The motions involved are analogous to rotations in the gas phase but are necessarily collective in nature in the liquid state. They are referred to as librations and can be treated, at least conceptually, by analogy with phonons in the solid state. Librational modes are characteristically of low frequency, $1-10 \text{ cm}^{-1}$, and can be treated as classical motions of the system at all but the lowest of temperatures.

Electron transfer in the normal region occurs from reacting partners which have those nonequilibrium solvent dipole and vibrational distributions appropriate for electron transfer to occur. There is a temperature dependence to electron transfer arising from the requirement to populate these nonequilibrium distributions.

The situation is quite different in the inverted region where $-\Delta G > \lambda$. If the energy released is far greater than λ , there is a changed role for the solvent. The factors that influence rates of electron transfer are the same as those for nonradiative excited state decay. The key is the ability of the system to release energy into the surrounding molecular vibrations when electron transfer occurs. A prediction of time dependent perturbation theory and quantum mechanics is that the energy release will be dominated by those modes of highest frequency which have significant changes in equilibrium displacement between the initial and final states.^{12,13} It is for those modes that maximum vibrational overlap exists between the initial and final states and they provide the major channel for the energy release associated with the excited to ground state transition. Typically, solvent modes do participate but only as a minor partner because of their classical nature. Rather, the solvent can play a major role by its effect on ΔG .³¹ As in excited state decay, the energy gap between the initial and final states is important since it determines the extent of vibrational overlap for the higher frequency modes.

These predictions are borne out and play an important role in light induced electron transfer. The intramolecular quenching

reaction in 4 provides an example. In fluid solution, $\text{Re} \rightarrow \text{bpy}$ excitation is followed by sub nanosecond intramolecular electron transfer. In a 1:1 ethanol/methanol (V:V) glass at 77 K, the $\text{Re} \rightarrow \text{bpy}$ emission is not quenched.

In addition to the flattening of the two rings of the pyridinium acceptor, the loss of solvent dipole mobility in the glass plays a major role. Compared to the ground state, there is a greater charge transfer distance in the Re-MQ^+ based state in reaction 4 compared to the initial Re-bpy MLCT state. This increases the contribution to λ_0 for this state and contributes to the inversion in the ordering of the Re-bpy and Re-MQ^+ states in the glass. The solvent dipoles can not reorient following $\text{Re} \rightarrow \text{bpy}$ excitation because they are frozen. Even $\text{Re} \rightarrow \text{MQ}^+$ excitation leads to Re-bpy based emission following the reverse electron transfer step in reaction 5.

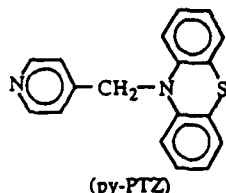
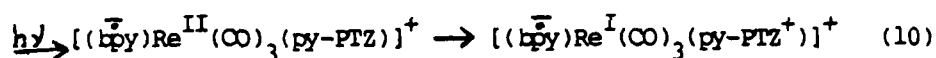
Intramolecular quenching can occur in the glass if the reaction is sufficiently spontaneous. This has been shown by Re-bpy MLCT quenching and the appearance of Re-MQ^+ based emission in the bpy-substituted complex $[(4,4'-(\text{NH}_2)_2\text{-bpy})\text{Re}(\text{CO})_3(\text{MQ}^+)]^{2+}$. The important criterion that must be met in order for quenching to occur in the glass is that $-\Delta(\Delta G) > \lambda_0$.²⁶ $\Delta(\Delta G)$ is the difference in excited state energies between the final ($\text{Re}^{\text{II}}\text{-MQ}^+$) and initial (bpyRe^{II}) excited states. $\Delta\lambda_0$ is the difference in solvent reorganizational energies between the Re-MQ^+ based state and the ground state and between the Re-bpy based state and the ground state.

Frozen solvent dipole effects also appear in nonradiative decay but they have a different origin. It is characteristic of MLCT excited states that their emissions shift to lower energies and nonradiative lifetimes shorten in the glass to fluid transition region.³² In a frozen glass, solvent dipole orientations are frozen. There is no way for reorientation to occur following excitation of the ground state. Emission is at high energy because the solvent dipoles have configurations appropriate to the ground state rather than the MLCT excited state. In fluid solution the dipoles can reorient following excitation and the emission is

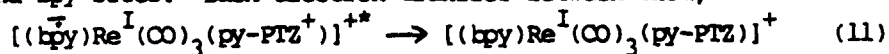
shifted to lower energy. Dynamically, the effect of solvent is indirect. It influences k_{nr} by its effect on the energy gap through eq. 1.³³ In fluid solution, rapid dipole relaxation occurs, the energy gap is lower, and the nonradiative decay rate increases.

Intermediate States. Multiple Electron Transfers. The lifetimes of the states which are the immediate products of intramolecular electron transfer quenching are themselves subject to the usual rules which dictate electron transfer and/or nonradiative decay. However, different kinds of states can be reached which differ in a fundamental way depending on the extent of electronic interaction between the electron transfer donor and acceptor sites. For example, intramolecular MQ^+ -based quenching in $[(bpy)Re(CO)_3(MQ^+)]^{2+}$ involves an intramolecular electron transfer from levels which are largely $\pi^*(bpy)$ in character to levels which are largely $\pi^*(MQ^+)$, reaction 4. Here, intramolecular electron transfer leads to an interconversion between excited states. The MQ^+ -based state which is reached is also a metal to ligand charge transfer excited state of the system. It emits in fluid solution at room temperature.^{23b} Its decay to the ground state by electron transfer from MQ^+ to $Re(II)$ is subject to the normal rules of nonradiative decay. They include the use of "promoting modes" to mix the excited and ground state electronic wave functions.^{12,13}

The situation is different if electronic coupling is weak. An example is shown in reaction 10. In reaction 10



initial $Re \rightarrow bpy$ excitation is followed by electron transfer from the -PTZ electron transfer donor to $Re(II)$. There is no orbital basis for strong electronic coupling between the photoproducted $-PTZ^+$ and bpy sites. Back electron transfer between them,



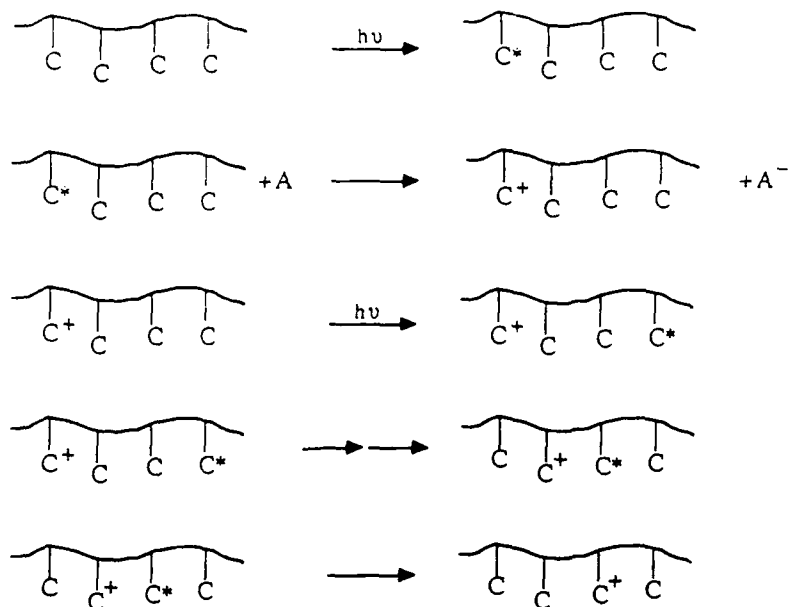
and excited state decay of $[(bpy)Re^{II}(CO)_3(MQ^+)]^{2+*}$ are related processes in that $\sim 2eV$ are released when back electron transfer occurs. In both cases the large energy release must appear in the surrounding molecular vibrations. However, decay of the $bpy-PTZ^+$ based state is an electron transfer process between sites that are weakly coupled electronically. The $bpy-PTZ^+$ state is not a true excited state of the system in that emission is not expected to occur. The matrix element that mixes the charge separated state with the ground state is the usual electrostatic operator of normal electron transfer.

In the conversion of light energy to chemicals, most of the attractive energy storage reactions, such as water splitting, involve multiple electron changes. Invariably, in these small molecule reactions, single electron steps lead to high energy intermediates such OH or H which are highly reactive and energetically unacceptable. This creates a problem for excited state-electron transfer based schemes. In all such schemes one photon produces one oxidizing equivalent and one reducing equivalent. There is, therefore, a requirement in a reactivity sense that the excitation-electron transfer apparatus be cycled more than once with the redox equivalents being stored for the following multielectron steps.

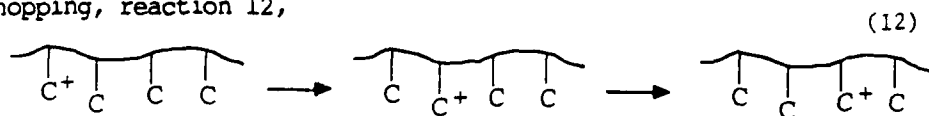
In Photosystem II a series of monophotonic events at the reaction center leads in a sequential fashion to the production and storage of multiple oxidative equivalents. The oxidative equivalents are transferred by electron transfer chains to the catalytic site where the oxidation of water occurs after four equivalents are accumulated.

In an artificial system the necessity for collecting and storing multiple redox equivalents also exists. One approach to the accumulation problem is to utilize ligand-bridged metal complexes or multiple redox sites bound to polymers. At first glance a fatal flaw appears to exist in such strategies. The flaw is illustrated for a polymer containing the multiple chromophoric sites C in Scheme 4.

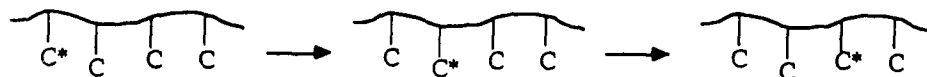
SCHEME 4



Excitation and quenching, in this case to an external acceptor A, would lead to a multichromophoric array which contains an oxidized site. Rapid electron transport amongst these sites via electron hopping, reaction 12,



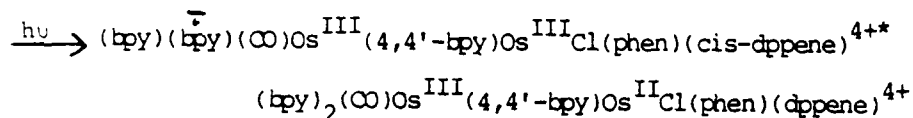
is a required property if redox equivalents are to be transported to a catalyst site. If electron transfer, or energy transfer, reaction 13,



between sites is facile, a basis exists for self-quenching by electron transfer as shown by the final reaction in Scheme 4.

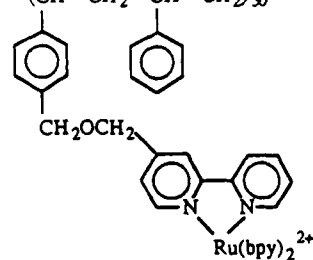
Typically such self-quenching reactions are highly favored thermodynamically. For example, the oxidative quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by $[\text{Ru}(\text{bpy})_3]^{3+}$ is favored by 2.1 eV. Because of the large energy release, self-quenching need not necessarily inhibit

the buildup and storage of multiple redox equivalents in a single large molecule. The same energy gap law which helps to dictate rates of nonradiative decay and electron transfer in the inverted region has an important role to play in self-quenching. This has been known for some time from studies on ligand-bridged mixed-valence complexes. For the complexes $[(bpy)_2(CO)Os^{II}(4,4'-bpy)Os^{III}Cl(phen)(cis-dppene)]^{4+}$ ²⁷ or $[(bpy)_2ClRu^{II}(4,4'-bpy)Ru^{III}(NH_3)_5]^{4+}$,³⁵ $Os \rightarrow bpy$ or $Ru \rightarrow bpy$ MLCT excitation is not followed by facile intramolecular electron transfer as in,

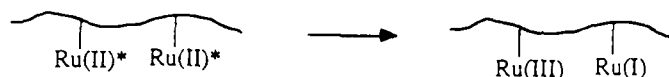


For the mixed-valence Os complex, intramolecular quenching is favored by > 2eV but it is slow. The quenching is slow because of the large energy release and the relatively weak coupling between $\overset{\cdot}{bpy}$ and the remote M(III) site in the initial excited state.

We have observed the same phenomenon in soluble polymers. In this work, we have attached Ru-bpy and Os-bpy chromophores to soluble 1:1 polystyrene/chloromethylpolystyrene polymers by nucleophilic displacement of the chloro groups.³⁶ Samples have been prepared in which complete substitution leads to as many as 30 Ru(II) or Os(II) complexes chemically attached to a single polymeric strand. The repeating structural unit is shown below, $-(CH-CH_2-CH-CH_2)_{30}-$



We have carried out lifetime and emission quantum yield measurements on these multiple light absorbers as a function of the relative content of M(II) and M(III). The degree of mixed-valence character can be adjusted by adding controlled amounts of chemical oxidants such as Ce(IV). In the pure M(II) containing polymers, multiple excitation and energy transfer does lead to a self-quenching pathway apparently via,



However, for the mixed-valence polymers we find that self-quenching of $M(II)^*$ by $M(III)$ does not play an important role.³⁷ The introduction of the potentially quenching $M(III)$ sites has, at best, a subtle effect on the excited state properties of the remaining $M(II)$ sites. The absence of self-quenching has allowed us to create and store as many as 30 oxidative equivalents on a single polymeric strand by sequential excitation/oxidative quenching steps by using the irreversible oxidative quencher $[Co(NH_3)_5Br]^{2+}$ in acidic solution.³⁷

Perspectives. The processes of importance in excited state electron transfer schemes depend upon the fundamental principles of chemistry and physics. From those principles, equations can be derived, which give quantitative or semiquantitative insight into quantum yields and rates. In turn, those equations are couched in terms of the molecular properties of the system. Between the underlying principles and an appropriate manipulation of properties, it does appear that it should be possible to dictate rates and quantum yields of charge separation in molecular systems in a systematic way.

In Table 1 an attempt has been made to summarize how such properties as energy gap, spin, and the solvent influence the various excited state processes which determine the efficiency with which MLCT excited states function in energy conversion schemes.

TABLE 1. RELATIONSHIPS BETWEEN EXCITED STATE PROCESSES AND MOLECULAR PROPERTIES FOR MLCT EXCITED STATES

Process	Role of Molecular Properties
nonradiative decay	<p><u>energy gap</u> - $k \propto \exp -(\gamma E/\hbar\omega)$. In this limit k decreases as the energy stored increases k also increases as the change in equilibrium displacement between the ground and excited states increases for the dominant acceptor modes.</p> <p><u>spin</u> - $k \propto \langle \psi_e \partial/\partial q \psi_g \rangle^2$. Spin-orbit coupling mixes singlet character into the excited state.</p> <p><u>solvent</u> - The solvent affects k indirectly through the energy gap, E, and slightly as a direct energy acceptor. Dynamic effects occur in the glass to fluid transition region.</p>
radiative decay	<p><u>energy gap</u> - $k \propto E^3$. k is predicted to increase with E^3 and the square of the transition dipole moment.</p> <p><u>spin</u> - $k \propto \langle \psi_e \vec{r} \psi_g \rangle^2$. The transition dipole moment can be evaluated from the integrated absorption band connecting the states. Spin-orbit coupling mixes singlet character into the excited state.</p>
electron transfer quenching	<p><u>energy gap</u> - $k \propto \exp - [(\lambda + \Delta G)^2 / 4\lambda RT]$ in the classical limit. k increases with $-\Delta G$. The reaction is barrierless at $-\Delta G = \lambda$. The inverted region occurs for $-\Delta G > \lambda$ at which point k decreases with $-\Delta G$.</p> <p><u>solvent</u> - Influences k via ΔG and λ ($\lambda = \lambda_i + \lambda_o$). Solvent dynamic effects may also contribute to ν_{et}. Electron transfer quenching in a frozen solution is inhibited unless $-\Delta(\Delta G_{ES}) > -\Delta\lambda_o$ and the reaction occurs in the inverted region.</p>
separation of redox equivalents following quenching	<p><u>energy gap</u> - If $-\Delta G > \lambda$, back electron transfer occurs in the inverted region and $k \propto$</p>

$\exp(-\gamma E/\hbar\omega)$. The greater the energy stored, the greater the efficiency of charge separation.
spin - If there is a spin change between the initial excited state and the final redox products, back electron transfer may be inhibited.
electrostatics - Coulombic repulsion between like charged quenching products increases the rate by which they separate which increases the efficiency of charge separation.

decay of intermediate states

energy gap - With sufficient energy stored, $-\Delta G > \lambda$ for excited state decay and $k \propto \exp(-\gamma E/\hbar\omega)$.
strong electronic coupling - $k_{nr} \propto \langle \Psi_e | \partial / \partial q | \Psi_g \rangle$. Emission may occur.
weak electronic coupling - $k \propto \sqrt{v_{et}}$.
 No emission.
by electron transfer - $k \propto \exp - [(\lambda + \Delta G)^2 / 4\lambda RT]$.

accumulation and storage
 redox equivalents

energy gap - Self-quenching by of adjacent oxidative or reductive sites may be slow if $-\Delta G > \lambda$; $k \propto \exp(-\gamma E/\hbar\omega)$.

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